

LUMINOPHORES BASED ON ALUMINUM YTTRIUM GARNET (REVIEW)

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The methods for synthesis and properties of luminophores based on aluminum yttrium garnets activated by rare-earth elements for LED sources of light are reviewed. The composition dependences of the spectral characteristics of the luminophores are presented.

Key words: aluminum yttrium garnet, luminescence spectrum, LED luminophore.

Luminophores for LED sources of light can be classed separately because they must meet certain requirements. The excitation wavelength must correspond to blue light, i.e., the excitation spectrum lies in a shorter-wavelength region than the radiation spectrum, since luminophores with anti-Stokes conversion (excitation in the long-wavelength region of the spectrum, radiation at shorter wavelengths) have a lower quantum yield. White LED sources of light based on diodes emitting in the UV region possess lower luminosity than those based on blue LED (the smaller the Stokes shift, the higher the quantum yield) and are characterized by a more complex composition of the luminescing mixture.

The temperature in LED illumination setups can rise above 150°C, as a result of which the LED luminophore must be stable at elevated temperatures. In addition, their afterglow must be short in order to ensure a fast transition from the excited state into the ground state with luminosity and subsequent excitation. For household LED sources of light the color temperature should correspond to day or evening sunlight so that the color index is greater than 80 and the setup must be environment friendly, safe and economically competitive in the lighting fixtures market.

The following are used as luminophores for LED sources of light: silicate luminophores, sialons, aluminate luminophores, phosphate, sulfide and selenide luminophores and garnets (aluminum-yttrium garnets, in which the activators are rare-earth elements, for example, cerium $\text{Y}_3\text{Al}_5\text{O}_{12} : \text{Ce}^{3+}$ (YAG : Ce) and their modifications. The quantum yield of the luminophore YAG:Ce is about 85%. Its advantages are weak thermal quenching and product manufacturability; the drawbacks are high color temperature, corresponding to the color of cold stars, and quite low color rendering index, about 70 – 80 [1]. The drawbacks of this luminophore have

stimulated the development of new YAG-based compositions directed toward correcting the luminescence spectrum and improving color rendering.

The basic stages in the production of YAG are preparation of the mixture of substances and synthesis at high temperatures. It is difficult to obtain a pure YAG phase because $\text{Y}_2\text{O}_3\text{--Al}_2\text{O}_3$ is a complex system with two intermediate compounds — aluminate with the perovskite structure YAlO_3 (YAP) and the monoclinic structure $\text{Y}_4\text{Al}_2\text{O}_9$ (YAM). Several phase transitions occur during heat treatment of the mixture of oxides Y_2O_3 and Al_2O_3 : $\text{YAM} \rightarrow \text{YAP} \rightarrow \text{YAG}$ [2]. During solid-phase sintering the YAG phase starts to precipitate at 1200°C, but pure YAG can be obtained up to 1600°C.

The components of the mixture can be prepared by different methods, e.g., sol-gel [3], co-precipitation [4], evaporation of a salt solution with carbamide [5] and spray drying [6].

The grain composition, grain surfaces and choice of subsequent synthesis regime depend on the method used to prepare the mixture. Methods such as sol-gel, evaporation with carbamide and co-precipitation can lower the sintering temperature from 1600 to 1000 – 1200°C compared with the standard solid-phase sintering of oxide mixtures. The next stage of synthesis is heating the mixture, soaking in a furnace at high temperature for several hours and cooling. In other cases a complex temperature regime with two soakings at the optimal temperature for nucleation and active growth. Fluxes, for example lithium salts, are added to obtain greater crystallinity and to increase grain size [7].

Hydrothermal synthesis of YAG at a lower temperature is possible. The process is conducted at elevated pressure (70 – 170 MPa) and temperature 500 – 600°C. Work has been done on the synthesis of aluminum-yttrium garnets under soft hydrothermal conditions at temperature 200 – 400°C and pressure 1.5 – 26 MPa [8].

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SPRAY DRYING

The initial materials are yttrium and aluminum oxide powders and cerium nitrate hexahydrate (Y_2O_3 , Al_2O_3 and $Ce(NO_3)_3 \cdot 6H_2O$) with NaOH as a flux. The initial materials in the ratio necessary to obtain $(Y_{3-x}Ce_x)Al_5O_{12}$ are comminuted in a ball mill, after which the mixture is placed into spray drier at $200^\circ C$. The granules obtained are fired at $1500^\circ C$ in a furnace for 8 h.

CO-PRECIIPITATION WITH AMMONIUM HYDROCARBONATE NH_4HCO_3

A mixture of salts containing yttrium, aluminum and cerium in the required molar ratio — $2.94Y : 5Al : 0.06Ce$ or $2.88Y : 5Al : 0.12Ce$ — is prepared. The solution is sprayed into the precipitator NH_4HCO_3 with continual mixing. After settling the suspension is filtered and washed with distilled water. Next it is dried at $100^\circ C$ and heated at temperature above $1000^\circ C$ in a CO atmosphere.

SOL-GEL METHOD WITH CITRIC ACID ($C_6H_8O_7 \cdot H_2O$)

A solution containing YAG-forming ions with the molar ratio $2.88Y : 4Al : 0.12Ce$ is prepared. The solution obtained is added in drops to a mixture of citric acid with ethylene glycol with continual mixing until the mixture becomes transparent. After heating and soaking at $200^\circ C$ for 5 h the color of the solution changes from pale-yellow to bright-yellow and then brown. When the excess solvent is removed the solution becomes more viscous without any precipitates or cloudiness. Subsequently, a dark-brown glassy substance reminiscent of resin is obtained. Next, the substance is fired at $400^\circ C$ for 2 h, which yields a dry, dark, hard mass. This mass is comminuted into powder and fired at $1000^\circ C$ in air.

EVAPORATION OF SALT SOLUTIONS WITH CARBAMIDE ($CO(NH_2)_2$)

A solution of salts containing yttrium, aluminum and cerium in the required molar ratio $2.94Y : 5Al : 0.06Ce$ or $2.88Y : 5Al : 0.12Ce$ is heated to boiling. Carbamide is added to the boiling solution. After prolonged heating and evaporation the solution becomes transparent and foams up into white foam. The foam is dried, comminuted and fired at $1000^\circ C$ in air for 5 h [9].

According to x-ray diffraction analysis $Y_3Al_5O_{12}$ has a cubic crystal lattice with space group Ia3d and cell constants $a = b = c = 12.0136(9) \text{ \AA}$. In the YAG structure Y occupies the 24(c) position with dodecahedral (distorted cubic lattice) crystal shape and coordination number 8. Al^{3+} appears in two forms in the lattice — octahedral 16(a) and tetrahedral 24(d) [10].

YAG acquires luminescence properties as a result of activation by rare-earth elements, for example, Y^{3+} ions are re-

placed by europium Eu^{3+} or cerium Ce^{3+} ions. Light absorption is due to an electronic transition of $Ce^{3+} 4f^1 \rightarrow 5d^1$ and emission is due to the reverse transition $5d^1 \rightarrow 4f^1$. The transition $4f^7 \rightarrow 4f^65d^1$ with excitation and the reverse with emission occur in trivalent europium.

A significant drawback of YAG:Ce is a deficit of a red spectral component in the luminescence, but the spectrum can be shifted into the red region by replacing Y^{3+} by Gd^{3+} or replacing Al^{3+} (octahedral) — Al^{3+} (tetrahedral) by Mg^{2+} – Si^{4+} . However, the quantum yield of the luminophore decreases in this case. The luminescence spectrum of YAG has been successfully adjusted by co-activation of YAG by trivalent cerium and praseodymium [11]. The latter ions contribute two sharp luminescence peaks at 609 and 611 nm and a weak line in the long-wavelength region of the red spectrum at 637 nm. An example of the composition of aluminum yttrium garnet co-activated with cerium and praseodymium is $(Y_{0.959}Ce_{0.04}Pr_{0.001})_3Al_5O_{12}$. The color coordinates were also adjusted by co-activation by Ce^{3+} and Sm^{3+} [12].

The base YAG can be modified over a wide range. Modified compositions of aluminum yttrium garnets with partial substitution of gadolinium ions for yttrium ions have been developed. Three stable compounds exist in the system Gd_2O_3 – Al_2O_3 : monoclinic gadolinium aluminate (GAM, $Gd_4Al_2O_9$), gadolinium aluminate in the perovskite structure (GAP, $GdAlO_3$) and aluminum gadolinium garnet (GAG, $Gd_3Al_5O_{12}$) [13]. The GAG phase exists only in the temperature interval $1200 - 1400^\circ C$. Pure aluminum gadolinium garnet is difficult to obtain. It is known that attempts to obtain YAG with a high content of gadolinium have been unsuccessful [14]. In the GAG system Gd^{3+} is partially replaced by Tb^{3+} , Y^{3+} or Lu^{3+} ions in one case and Al^{3+} is replaced by Gd^{3+} in another case. The crystal structure of GAG ($Gd_3Al_5O_{12}$) and gallium-yttrium garnet ($Y_3Ga_5O_{12}$) is cubic with cell constants $a = 12.11 \text{ \AA}$ and $a = 12.27 \text{ \AA}$, respectively. When Al^{3+} is replaced by Ga^{3+} in the luminophore $Y_{2.7}(Al_{1-y}Ga_y)_5O_{12} : Ce_{0.3}$ the lattice parameter increases from $a = 12.01 \text{ \AA}$, as in pure YAG, to $a = 12.27 \text{ \AA}$ for $y = 0.8$, since the ionic radius of Ga^{3+} (0.62 \AA) is greater than that of Al^{3+} (0.51 \AA). As the Ga content increases, the emission spectrum shifts into the short-wavelength region and the intensity decreases compared with YAG : Ce.

On replacing Y^{3+} by Gd^{3+} ($Y_{1-x}Gd_x$) $_2.7Al_5O_{12} : Ce_{0.3}$ the lattice parameter a also increases, since the ionic radius of Gd^{3+} (0.94 \AA) is greater than that of Y^{3+} (0.90 \AA). The emission spectrum shifts into the long-wavelength region with higher Gd^{3+} content [15].

On replacing Gd^{3+} by Lu^{3+} ions with a smaller ionic radius in GAG : Ce the luminescence spectrum shifts into the blue region [16]. Conversely, when the Y^{3+} ions were replaced by Gd^{3+} or La^{3+} the luminescence spectrum shifted into the long-wavelength region.

The position of the luminescence spectrum depends on the environment of the Ce^{3+} ion, which is explained by the $Re-O-Ce$ bond ($Re = Gd^{3+}$, replaced by Lu^{3+}). The ionic

bond $Re-O$ decreases with increasing Lu concentration, since the electronegativity of lutetium ($\chi_{Lu} = 1.27$) is higher than that of gadolinium ($\chi_{Gd} = 1.20$) [17]. If an ion with high electronegativity, such as Lu^{3+} , is present in the crystal lattice next to an activator center, the ionicity of the $Lu-O$ bond decreases (the ionicity of the $Lu-O$ bond is less than that of $Gd-O$), which increases the ionicity of $O-Ce$. Such a shift of the luminescence spectrum is observed when Ga^{3+} is implanted in GAG. For the $Me-O-Ce$ bonds ($Me = Al$, replaced by Ga) the electronegativity of gallium ($\chi_{Ga} = 1.81$) is higher than that of aluminum ($\chi_{Al} = 1.61$). The ionicity of the $Me-O$ bond decreases with increasing Ga content, which increases the strength of the $O-Ce$ bond in $Me-O-Ce$, and the luminescence spectrum shifts into the blue region. As a result of the replacement of Gd^{3+} by Lu^{3+} the ionicity of the $O-Ce$ bond increases, Ce^{3+} absorbs the energy of the transition $4f \rightarrow 5d$ and its losses decrease, which is expressed as a shortening of the distance between the absorption and emission peaks [18].

Luminophores based on aluminum terbium garnets (TAG : Ce), whose spectrum is shifted very little into the red region compared with YAG : Ce, are also widely used. Efficient co-activation of the TAG base by Ce^{3+} and Eu^{3+} ions is possible. In such a system active absorption of the exciting radiation by the Tb sublattice occurs, while Ce effectuates energy transfer to Eu^{3+} ions. Owing to this better color rendering and luminescence properties of the luminophore are observed [19]. Efficient TAG luminophores have been developed; their compositions can be expressed by the general formula $(Tb_{1-x-y}Re_xCe_y)_3(Al, Ga)_5O_{12}$, where $Re = Y, Gd, La$ and/or Lu , $0 \leq x \leq 0.5 - y$, $0 < y < 0.1$. An example of a luminophore based on aluminum terbium garnet for LED light sources is $(Y_{0.50}Gd_{0.45}Tb_{0.01}Ce_{0.04})_3Al_5O_{12}$, whose luminescence spectrum is shifted into the red region compared with YAG [20].

As an example we present below the compositions of luminophores with garnet structure and the wavelengths of their emission peaks:

$(Y_{2.93}Ce_{0.07})Al_5O_{12} - 530 \text{ nm}$;
 $(Y_{0.94}Tb_{0.05}Mg_{0.01})_3Al_5O_{12} - 540 \text{ nm}$ [21];
 $(Y_{0.95}Ce_{0.05})_3Al_5O_{12} (Lu_{0.95}Ce_{0.05})_2O_3 - 583 \text{ nm}$;
 $(Y_{0.995}Ce_{0.005})_3Al_5O_{12} (Lu_{0.99}Ce_{0.01})_2O_3 - 590 \text{ nm}$;
 $(Y_{0.9}Ce_{0.1})_3Al_5O_{12} (Lu_{0.9}Ce_{0.1})_2O_3 - 593 \text{ nm}$;
 $(Y_{0.760}Gd_{0.20}Lu_{0.01}Ce_{0.03})_3Al_{4.98}Li_{0.001}Mg_{0.01}Si_{0.02}O_{11.98} \times F_{0.01}N_{0.01} - 596 \text{ nm}$;
 $(Y_{0.80}Gd_{0.15}Lu_{0.02}Ce_{0.029}Pr_{0.001})_3Al_{4.96}Me_{0.015}Si_{0.015}Li_{0.01} \times O_{11.98}F_{0.01}N_{0.015} - 611 \text{ nm}$ [22];
 $Ca_3Sc_2Si_3O_{12}(CSS) : Ce^{3+}, Mn^{2+} - 515 \text{ nm}$ [23];
 $Lu_3Al_5O_{12} : Ce - 535 \text{ nm}$ [24];
 $Y_3Ga_{0.1}Al_{4.9}O_{12} : Ce - 550 \text{ nm}$;
 $CaY_2Al_4SiO_{12} : Ce^{3+} - 550 \text{ nm}$ [25];
 $Y_3Al_5O_{12} : Ce^{3+}, Pr^{3+} - 555, 610, 635 \text{ nm}$ [26];
 $Tb_3Al_5O_{12} : Ce - 575 \text{ nm}$;
 $Y_3Mg_2AlSi_2O_{12} : Ce^{3+} - 600 \text{ nm}$.

Luminophores with the garnet structure can be denoted by the general formula $(Tb_{1-x-y}A_xRe_y)_3D_zO_{12}$, where $A = Y, La, Gd$ or Sm ; $Re = Ce, Pr, Nd, Sm, Eu, Gd, Dy, Ho, Er, Tm, Yb$ or Lu ; and, $D = Al, Ga$ or In .

This review has shown that a large number of luminophore compositions based on garnets, specifically, YAG, have been developed, and the properties of the new luminophores can be predicted. For example, the luminescence spectrum can be shifted by replacing dodecahedral yttrium by atoms of comparable size. On replacement by more electronegative atoms the luminescence spectrum shifts into the short-wavelength region and on replacement by less electronegative atoms it shifts into the long-wavelength region. This is explained by the fact that the more electronegative atom attracts to itself the electronic density in the chain $Re-O-Ce$, the $O-Ce$ bond becomes more ionic, the $4f \rightarrow 5d$ transition of the Ce^{3+} ion is facilitated and energy losses decrease, which is expressed as a reduction of the Stokes shift.

A similar principle can be used for the replacement of octahedral and tetrahedral aluminum: on replacement by more electronegative atoms the luminescence spectrum shifts into the long-wavelength region. At the same time, the greater the distance between the excitation and luminescence peaks, the lower the quantum yield is, and as a result the modified YAG luminophores must be chosen very carefully when designing LED illumination setups with high color rendering and luminosity. In addition, other methods of enriching the spectral properties of radiation exist, for example, multicomponent luminescence mixtures or polychromatic LEDs can be used.

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